

Propagation of surface deformation coupled with convection waves under the excitation of a chemical wave train

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Oscillation of surface deformation synchronized with oscillation of convection was found in a thin solution layer of a Belousov-Zhabotinsky reaction in which a spiral wave train was excited. To clarify the underlying mechanism of establishing oscillatory convection in the system, we measured the velocity of the convective flow at the surface and the angle of the surface tilt of the solution simultaneously. The convection and surface deformation showed propagation behavior. The propagating waves had a long wavelength (more than 100 μm) and a rapid propagation velocity (about 2.5 mm/s) compared to those of a chemical wave train. [S1063-651X(97)51309-2]

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INTRODUCTION

Recently, increased attention has been focused on chemically driven convection. It has been clarified that hydrodynamic flows can be directly induced by chemical waves in an adiabatic vertical tube and in a horizontal tube containing an iodate-arsenous acid system and a Mn^{2+} -catalyzed Belousov-Zhabotinsky (BZ) system [1–3]. In these systems, density-driven convection or Rayleigh-Bénard instability plays a role [2]. On the other hand, in a thin solution layer of an Fe^{2+} -catalyzed BZ reaction [4,5], interest is increasing in exotic and complex pattern dynamics caused by interaction between a reaction-diffusion process and Marangoni convection.

Mosaic patterns and stationary structures, caused by Marangoni-type convection due to evaporative cooling from the surface of a BZ solution layer, were observed in an uncovered dish [6–8]. This nonintrinsic effect can be suppressed by covering the dish. Convection directly induced by chemical waves have been reported by Miike *et al.* in a thin BZ-solution layer under a covered dish using small suspended particles under an inverted microscope [9,10]. They found that the flow direction oscillated in the thin solution layer when a chemical wave train of the order of 1 mm wavelength spread from the spiral center all over the petri dish. They also found oscillatory deformation of the propagating chemical wavefronts: the deformed wave profiles became sharp when the directions of the chemical wave and the surface flow were parallel, while the profiles became broad when the directions of the chemical wave and the surface flow were antiparallel. Matthiessen and Müller [11] visualized a global two-dimensional structure of the oscillatory flow traveling through the dish towards the spiral center using the differences in light transmission caused by the oscillatory deformation of the wavefronts. Recently, we found a periodic initiation of a moving structure of convection from the collision line of the fronts of two spiral wave trains excited in the layer [12]. The structure of the convection propagated toward the respective centers of the spirals and was annihilated at the centers.

On the other hand, traveling convection associated with

ordinary trigger waves [9] and a vigorous convection associated with a chemical wave having an acceleration of propagation velocity, a so-called big wave [13,14], have been reported. The flow velocity of convection induced by the big wave was 3000 $\mu\text{m/s}$, 30 times faster than one induced by an ordinary trigger wave. Recently, Matthiessen *et al.* investigated numerically the mechanism of chemically driven convection with the assumption of an undeformable surface [15]. They considered surface tension gradients generated by the nonuniformity of concentration of the catalyst ferroin as a driving force. The calculation agrees well with experimental data for a flow induced by an ordinary trigger wave that has a constant velocity of propagation. Kai *et al.* measured the surface deformation induced by a big wave in the solution layer using Mach-Zehnder interferometry [16–18]. They suggested that the convections in the thin BZ-solution layer are induced by a Marangoni instability caused by surface tension gradients. Especially, a long-scale Marangoni instability may play a role in the excitation of the big wave, which is accompanied by traveling convection.

Two types of Marangoni convection are known. They are a short-scale convection and a long-scale deformational Marangoni wave [19]. The characteristic scale of the Marangoni convection patterns without surface deformation, short-scale patterns, is of the same order of magnitude as the solution layer depth. On the other hand, a typical wavelength of long-scale Marangoni convection with surface deformation is large compared to the solution layer depth. The long-scale Marangoni convection has not been well studied compared to investigation of density-driven convection (Rayleigh-Bénard instability) and the short-scale Marangoni convection without surface deformation.

In spite of many experimental and theoretical studies [2,15,20–22], there is no satisfactory understanding of the mechanism of these curious phenomena such as the big wave and the oscillatory convection. In this study, we measured both the velocity of convection and the deformation of the surface to clarify how the oscillatory flow occurs in the thin BZ-solution layer where a chemical wave train is excited. We found oscillatory surface deformation in the layer. The deformation having a long wavelength was synchronized well with the direction of convection near the surface. Based

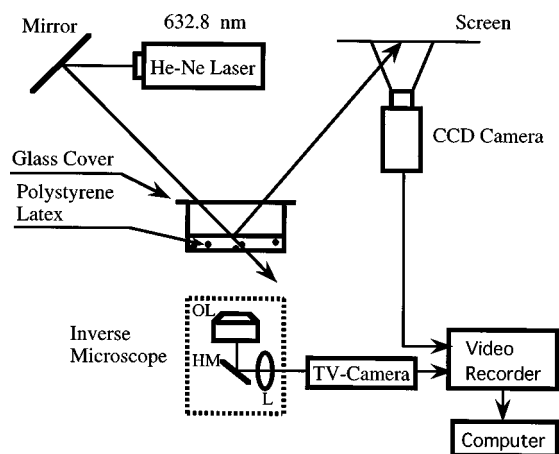


FIG. 1. Schematic diagram of the microscope video imaging system for the observation of convection and surface deformation.

on the results, we propose a picture of propagating surface deformation and convection waves having a long wavelength driven by long-scale Marangoni instability.

EXPERIMENT SETUP

The oscillatory BZ solution having a long period, which remains excitable for about 15 min, was placed in an optically flat circular petri dish 68 mm in diameter with a layer thickness of about 0.85 mm at room temperature $25 \pm 1^\circ\text{C}$. A circular wave was triggered by locally exciting the solution with a silver wire. Breaking of the wave front led to a chemical twin spiral center. The location of the center was about 10 mm away from the edge of the dish. The dust- and scratch-free dish, excluding CO_2 bubbles and other uncontrolled chemical waves, was covered with a glass plate to prevent evaporation. The air gap between the layer surface and the glass cover was 12 mm. The initial concentrations of the solution were 48 mM NaBr, 340 mM NaBrO_3 , 95 mM $\text{CH}_2(\text{COOH})_2$, 378 mM H_2SO_4 , and 3.5 mM ferroin.

Figure 1 shows a sketch of the microscope image sequence processing system for the observation of hydrodynamic flow and surface tilt. We mixed polystyrene particles of $0.46 \mu\text{m}$ in diameter with a BZ solution. A He-Ne laser illuminated the center of the surface of the solution at a slightly tilted angle for visualization of the motion of the polystyrene particles under an inverted microscope (Nikon DIAPHOT-TMD). A television camera capturing the motion of the polystyrene particles through the scattering light was focused on the surface. We measured the velocity of hydrodynamic flow by tracing the motion of the particles in a video movie.

The design of the measurement system for the surface tilt angle is described in Fig. 2. When the local surface of a point O is flat, the reflected light arrives at point A on the screen. If point O tilts, the arrived point moves from A to B on the screen. The local tilt angle β is represented as a function of the increment δd , that is, the distance AB

$$\beta = \frac{1}{2} \left\{ \tan^{-1} \left(\frac{p}{d} \right) - \tan^{-1} \left(\frac{p}{d + \delta d} \right) \right\}, \quad (1)$$

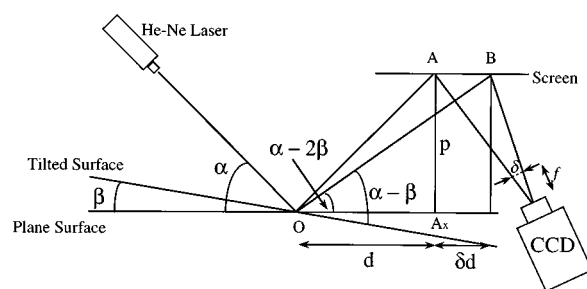


FIG. 2. Schematic diagram of the measuring system. Surface tilt angle is estimated by measuring the displacement δd of specularly reflected laser light, where d and p are 2.79 and 1.48 m, respectively.

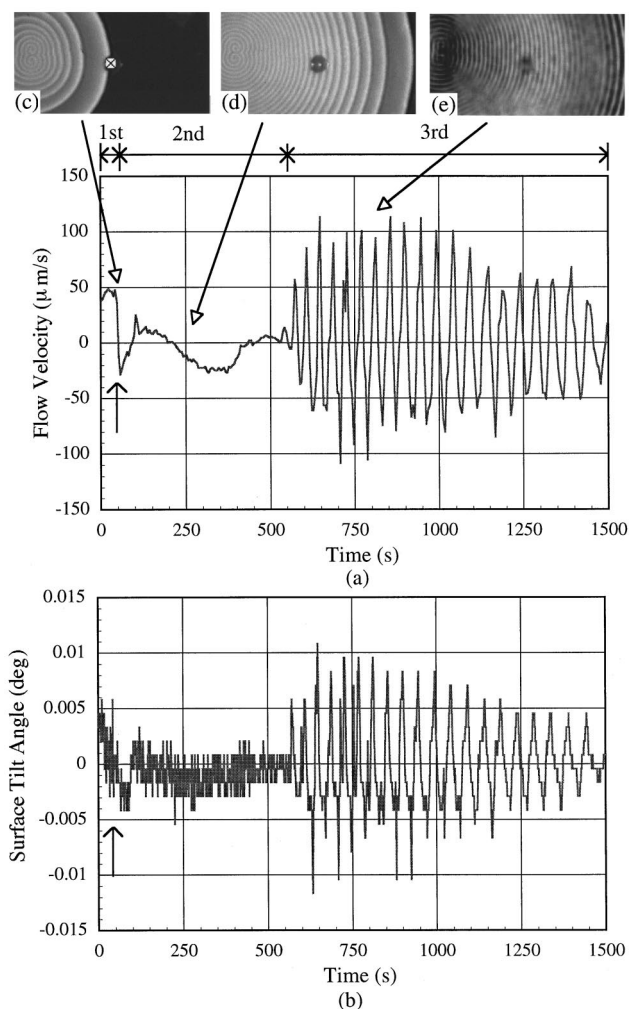


FIG. 3. Temporal evolution of the convection velocity (a) and the local tilt angle (b) measured near the surface of a BZ-solution layer at the center of a petri dish. Propagation of a spiral wave train induced oscillatory convection and oscillatory deformation of the surface. (c), (d), and (e) are image samples observed at about 50, 250, and 800 s, respectively. The position marked \times in (c) indicates the location of measurements of flow velocity and surface tilt angle with He-Ne laser illumination. (e) is an enhanced image using an image sequence processing method to visualize the convection wave and underlying chemical waves.

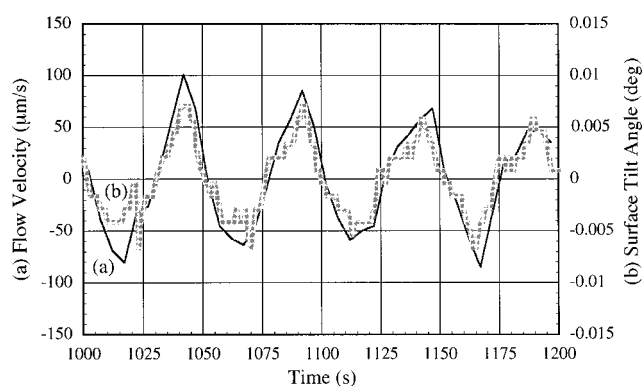


FIG. 4. Comparison between the convection velocity (a) and the local tilt angle of the solution surface (b) corresponding to the time duration between 1000 and 1200 s in Fig. 3.

where d is the distance from the reflection point O to point A_x and p is the distance from A_x to A . The d and the p were fixed at 2.79 and 1.48 m, respectively, in this experiment. The angle β is a function of time as δd varies with time. We measured both the velocity of surface flow and the deformation of the surface at the center of the petri dish simultaneously using two cameras and a special video recorder (SHARP, VC-BF80), which permits recording two movies in the same frame.

RESULTS

Figure 3(a) shows a temporal trace of convective flow velocity near the surface of the solution layer. The behavior of the measured flow is separated roughly into three stages, i.e., from 0 to 50 s, from 50 to 550 s, and from 550 to 1500 s. In the first stage, when the first chemical wave was approaching the observation area (\times) in Fig. 3(c), the flow direction was towards the wavefront. We defined this direction, that is, from the observation point to the spiral center, to be positive in Fig. 3(a). The flow direction suddenly changed in the passage of the first wave in every experiment at about 50 s (at \uparrow in Fig. 3). The first wave propagated into a relatively well-reduced medium; therefore, the behavior of the convective flow was similar to that of the flow induced by a single circular wave [9]. In the second stage, the distance between the wavefronts of the spiral wave train decreased from 10 to 1 mm as ten or more waves passed the observa-

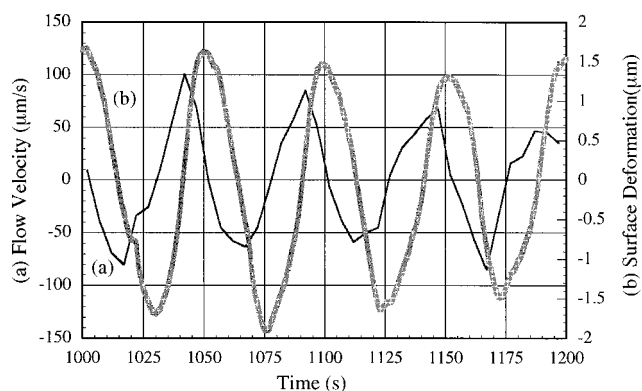


FIG. 5. Comparison between the convection velocity (a) and the surface deformation (b) obtained by Eq. (2).

tion area, as shown in Fig. 3(d). Because the spiral wave train propagated into a less reduced medium than the first stage due to the short wavelength, the velocity of the induced flow decreased with time. In this stage, there was no correlation between the chemical wave passage and the flow direction. After 550 s, however, the flow suddenly started to oscillate with a large amplitude of flow velocity, up to 100 $\mu\text{m/s}$, and the oscillation continued for more than 900 s (the third stage). In this stage, the flow direction changed synchronously with each passage of the chemical waves [9]. Figure 3(e) shows an example of a snapshot at about 800 s. The global bright region indicates the presence of a convection wave with a flow direction antiparallel to that of the chemical wave propagation [11,12]. Figure 3(b) shows a temporal trace of the surface tilt angle. The behavior of the surface tilt was synchronized well with the flow oscillation. Figure 4 corresponds to the time from 1000 to 1200 s in Figs. 3(a) and 3(b). The phase of maximum flow velocity almost agrees with the phase of maximum surface tilt angle.

An interesting question is how the surface deformation correlates closely with the induced surface flow. The surface deformation is evaluated from the change in the local tilt angle β , which is given by Eq. (1) under the condition that the surface deformation moves with a constant velocity v_d . Because the change in deformation is given by the product of the tangent of the angle β and the velocity v_d , we obtain a temporal trace of the surface deformation $h(t)$,

$$h(t) = \int_0^t v_d \tan \beta(t) dt. \quad (2)$$

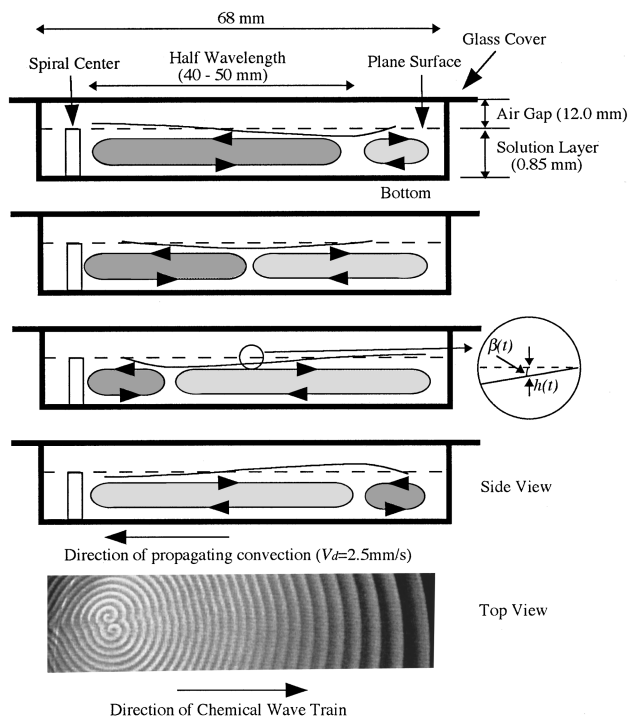


FIG. 6. Possible scheme for the oscillatory flow caused by a spiral wave train. The convection wave having a long wavelength with a long-scale surface deformation propagates through the edge of the dish towards the spiral center. The amplitude of surface deformation is about 2.0 μm . The half wavelength and propagation velocity of the surface deformation of the convection wave are about 60 mm and 2.5 mm/s, respectively.

To estimate the value of v_d , we measured the tilt angles at two points, where the distance was 7.5 mm, using two laser lights at the same time. The lag of the period of oscillation between two points was 3.0 s; therefore, the value of v_d was 2.5 mm/s, which is about 20 times the velocity of chemical waves. Figure 5 shows the deformation $h(t)$ and the velocity of oscillatory flow near the surface corresponding to Fig. 4. The surface deformation strongly correlates with the flow velocity. The maximum deformation of the solution layer in the oscillatory region, which is about 2.0 μm , is formed when the flow velocity become zero. We can estimate that the half wavelength of surface deformation is between 50.0 and 62.5 mm from the velocity of surface deformation ($v_d = 2.5$ mm/s) and the period of the oscillation ($T = 40 \sim 50$ s).

CONCLUDING REMARKS

In this study we reported that the oscillatory flow was closely correlated with the oscillatory surface deformation having a long wavelength which appeared in a thin solution layer of the BZ reaction under the excitation of a spiral wave train. Very recently, a global flow wave having a fast propagation velocity and a long wavelength was reported by Matthiessen and Müller [11] and Sakurai *et al.* [12]. Taking

these experimental results into account, we can conclude that the global structure of convection having a periodic surface deformation (maximum deformation is about 2.0 μm) propagates with a constant velocity (2.5 mm/s) through the edge of the dish towards the spiral center as shown in Fig. 6. This can be a possible scheme to explain the oscillatory convection and the oscillatory surface deformation appearing in the well-developed spiral structures in the BZ reaction. The Marangoni instability, having a long-scale surface deformation caused by nonuniform surface tension associated with chemical waves, may play an important role in establishing these curious pattern dynamics observed in a reaction, diffusion, and convection system. It is expected to clarify the relationship between the two-dimensional structure of the surface deformation and that of the convection waves. A numerical study using a model considering nonlinear coupling between reaction-diffusion and convection with a deformable surface is strongly encouraged.

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